

PATENT SPECIFICATION

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(54) PTC COMPOSITIONS AND DEVICES COMPRISING THEM

(71) We, RAYCHEM CORPORATION, a Corporation organized under the laws of the State of California, United States of America, of 300, Constitution Drive, Menlo Park, California 94025, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to conductive polymer compositions which exhibit positive temperature coefficient (PTC) behaviour, to devices containing such compositions and to methods of using such compositions.

Conductive polymer compositions comprise a conductive filler, usually carbon black, dispersed in a polymer. When the polymer is a thermoplastic crystalline polymer and contains a suitable amount of a suitable conductive filler, the composition exhibits PTC behavior, i.e. a sharp increase in resistivity over a particular temperature range, the increase beginning around the softening point of the polymer. Such compositions, have been used for example in self-limiting strip heaters, and have been cross-linked by irradiation at room temperature to improve their form stability at higher temperatures. Although there have been reports of PTC behavior in conductive polymers in which the polymer is not a thermoplastic crystalline polymer, it has been accepted by those skilled in the art that in order to obtain a practically useful PTC composition the conductive filler must be dispersed in a thermoplastic crystalline polymer and that the sharp increase in resistivity always takes place at or near the crystalline melting point of the polymer (see for example the article by J. Meyer in Polymer Engineering and Science, November 1973, 13 No. 6, pages 462—468).

As examples of the prior art relating to PTC compositions, reference may be made to U.S. Patents Nos. 2,978,665; 3,243,753; 3,412,358; 3,591,526; 3,793,716; 3,823,217; and 3,914,363; British Patent No. 1,409,695; Brit. J. Appl. Phys, Series 2, 2, 567—576 (1969, Carley Read and Stow); and Kautschuk und Gummi II WT 138—148 (1958, de Meij); as well as the Meyer article referred to above, the disclosures of which are hereby incorporated by reference. For details of recent developments in this field, reference may be made to German Offenlegungsschriften Nos. 2,543,314.1, 2,543,338.9, 2,543,346.9, 2,634,999.5, 2,635,000.5, 2,643,931.5, 2,643,932.6 and 2,655,543.1 and German Gebrauchsmuster No. 7,527,288.

We have now discovered that, provided a sufficient degree of cross-linking is introduced, the cross-linking of any conductive polymer (whether crystalline or amorphous, and whether previously cross-linked or not) will have a substantial effect on the resistance/temperature characteristics of the composition at a temperature which is related to the cross-linking temperature (which is frequently referred to herein as T_c), and/or at a temperature which is related to the temperature at which the polymer has previously been cross-linked. Thus such cross-linking frequently will cause the composition to exhibit useful PTC behavior



5 at a temperature related to T_c or will enhance previously existing useful PTC behavior around T_c . We have also found that the relation between T_c and the temperature range over which the effect (on resistance/temperature characteristics) is chiefly observed is, in the case of amorphous polymers, often at least in part dependent on the arrangement of the polymer chains at the time at which they are cross-linked. For example, if a polymer having high green strength is annealed at one temperature and is then heated (or cooled) to another temperature, both temperatures being above the melting point, and immediately cross-linked to an adequate extent, a PTC effect will be observed commencing at a temperature between the annealing temperature and T_c . On the other hand if the polymer has low green strength, the effect will commence near T_c . For crystalline polymers which are cross-linked at temperatures within the melting range, and which have preferably been allowed to equilibrate at T_c prior to cross-linking, different effects will be observed depending upon whether T_c is below or above about the peak of the crystalline melting range; thus when T_c is above the peak of the crystalline melting temperature, and the composition is sufficiently cross-linked, it will exhibit PTC behavior in two temperature ranges, the lower related to the crystalline melting point and the higher related to T_c . Yet different effects will be observed for crystalline polymers which are cross-linked below the peak of the crystalline melting range. We have also found that if a PTC composition is produced by a process which comprises two cross-linking steps carried out at different temperatures, the resistance/temperature characteristics can reflect either one or both of the cross-linking steps.

10 From the foregoing it will be clear that the present invention provides PTC compositions which have physical properties and/or resistance/temperature characteristics which have not previously been available. For example the invention makes it possible to prepare PTC compositions which (a) exhibit PTC behavior which is not associated with a first or second order thermodynamic transition of the polymer, e.g. the glass transition point or the crystalline melting point, or with chemical instability (this term being used to include, for example, a lessening of the rigidity of the cross-linked network above a certain temperature due to the lability of the cross-links above that temperature, e.g. the lability of disulfide links above about 70°C); or (b) have more than one useful T_s , preferably separated by at least 25°C, often by at least 50°C; or (c) exhibit PTC behavior which is associated with a thermodynamic transition of the polymer (as is known) but show sharper increases in resistivity than have hitherto been attained with the same polymer and same conductive filler.

15 In further describing and defining the present invention, the following terms and abbreviations are used in the ways defined below.

20 The gel fraction of a cross linked polymer is the weight fraction of the cross-linked polymer that is not soluble in a solvent for the uncross-linked polymer.

25 The term "switching temperature" (usually abbreviated to T_s) is used herein to denote a temperature range over which a PTC composition shows a rapid increase in resistivity, and is defined as the temperature at which extensions of the substantially straight portions of the plot of the log of the resistance against the temperature (above and below the range) cross. In order to be practically useful, a PTC composition must have at least one T_s which is between about -100°C and about 250°C, and which is associated with a temperature range in which the composition has an R_{14} value of at least 2.5 or an R_{100} value of at least 10 (and preferably both), where R_{14} is the ratio of the resistivities at the end and beginning of a 14°C range and R_{100} is the ratio of the resistivities at the end and beginning of a 100°C range. It is also a practical requirement that the resistivity is below about 10^5 ohm. cm. at the beginning of that temperature range. The term "critical range" is used herein to denote a temperature range in which the R_{14} value is at least 2.5 or the R_{100} value is at least 10, and at the beginning of which the resistivity is below about 10^5 ohm. cm. A PTC composition is described herein as "having a useful T_s " if a plot of its resistivity against temperature shows a critical range (as defined above) which gives rise to a T_s between -100°C and +250°C. The term "Peak Resistivity" is used herein to denote the maximum resistivity of the composition as it is heated to temperatures beyond any useful T_s , and the temperature at which the composition shows its peak resistivity is called the "Peak Temperature". The ratio of the Peak Resistivity to the resistivity at the useful T_s (or at the highest useful T_s if there is more than one) is called the Peak Ratio. As will be apparent from the discussion, a composition having a T_s is one which over the temperature range

under consideration has a positive temperature coefficient of resistivity, i.e., it is a PTC composition. A PTC element is a structure comprising such a composition.

In one aspect, the present invention provides a composition which comprises

(1) a cross-linked polymer; and

(2) conductive particles enclosed within the cross-linked network of the polymer, the particles having a size of at least 18 millimicrons;

the polymer of which composition has a gel fraction of at least 0.6 and which composition has at least one useful T_g , subject to the proviso that when the cross-linked polymer comprises a cross-linked crystalline polymer and the composition had a useful T_g prior to cross-linking, the cross-linked composition has at least two useful T_g values, preferably having one which is above the useful T_g of the composition prior to cross-linking. The composition preferably has at least one useful T_g between 25°C and 200°C. The resistivity of the composition will for many applications preferably be at least 25 ohm. cm. at the higher of 25°C and a temperature 50°C below the useful T_g (or the lowest useful T_g if there is more than one). Especially when the composition is used at low voltages, the resistivity at 25°C can be low, for example 1 ohm. cm. or lower, though it is preferably at least 3 ohm. cm., especially at least 5 ohm. cm. It is preferred that the critical range of the composition (or at least one of the critical ranges when the composition has more than one useful T_g) should have an R_{30} value of at least 6, where R_{30} is the ratio of the resistivities at the end and beginning of a 30°C range. Another preferred feature is that the (or each) useful T_g of the composition should remain substantially unchanged when the composition is repeatedly subjected to thermal cycling which comprises heating the composition from a temperature below the useful T_g to a temperature above the useful T_g but below the Peak Temperature, followed by cooling to a temperature below the useful T_g . It is also preferred that the Peak Ratio is at least 20:1, especially at least 100:1. It is further preferred that when the useful T_g is less than 150°C, the ratio of the resistivity at 200°C to the resistivity at T_g is at least 20:1; and that when the useful T_g is greater than 150°C, the ratio of the resistivity at 250°C to the resistivity at T_g should be at least 20:1.

In the compositions of the invention the cross-linked polymer can be a mixture of cross-linked polymers and the composition may include other components such as fillers, flame retardants and antioxidants, as well as other cross-linked polymers not having conductive particles enclosed within the cross-linked network thereof, and thermoplastic amorphous or crystalline polymers which may or may not have conductive particles mixed therewith.

The invention also includes a process for making the composition as defined above, which process comprises:

(1) dispersing conductive particles having a size of at least 18 millimicrons in a polymer (this term being again used to include a mixture of polymers); and

(2) cross-linking the dispersion from step (1) to obtain a composition which has a gel fraction of at least 0.6 and which comprises conductive particles enclosed within the cross-linked network of the polymer;

the particles, the polymer, and the cross-linking conditions being such that the cross-linked composition has at least one useful T_g , subject to the proviso that when the polymer comprises a crystalline polymer and the composition has a useful T_g prior to cross-linking, the cross-linking is effected in two stages carried out at substantially different temperatures or is effected under conditions such that the cross-linked composition has a useful T_g above the useful T_g of the composition before cross-linking. When the polymer comprises a crystalline polymer, the cross-linking is preferably effected under conditions such that the cross-linked composition has a first useful T_g near the crystalline melting point of the polymer and a second useful T_g near the temperature of the cross-linking step.

In one embodiment of the process, the cross-linking is effected in two stages carried out at substantially different temperatures. When the polymer is a thermoplastic it is usually preferable that the first cross-linking should be effected at lower temperature than the second. When the cross-linked polymer is an elastomer it is generally preferable the first cross-linking should be effected at a higher temperature than the second.

The invention is illustrated by the accompanying drawings, in which the Figures show the relation between resistance and temperature of various PTC compositions according to the invention, as further described in the Examples below.

The invention further provides a device, e.g. a strip heater, comprising a PTC element and at least one electrode, generally two electrodes which can be connected to a source of electrical power (e.g. D.C. from one or more 12 volt batteries or AC from a 110 or 220 volt source) to cause current to flow through the PTC element, wherein the PTC element comprises a PTC composition as defined above. As discussed in detail in German Offenlegungsschrift No. 2,543,314.1 and in German Gebrauchsmuster No. 7,527,288, a problem which has frequently arisen in the operation of PTC devices is the formation of so-called "hotlines", that is the formation of a narrow band in the PTC material which is at a higher temperature than the surrounding PTC material. In the devices of the invention, the current preferably flows through the PTC element in a way which substantially prevents the formation of hotlines. Thus one preferred device is in the form of a strip heater comprising two parallel spaced-apart electrodes which are separated by a distance d (e.g. of 0.15 to 1 cm.) and are enclosed within a web of the PTC composition, the portion of the web between the electrodes having a minimum thickness t which is greater than the maximum dimension of the electrodes in the same direction and is such that d/t is less than 9, preferably less than 7, especially less than 5, particularly 3 to 4. In another type of preferred device, the PTC composition is in the form of a layer and the electrical connections thereto are such that, at least when the layer is at or near T_s , the current flow is predominantly through the thickness of the layer. Especially when the polymer in the PTC composition is an elastomer, such layers can be relatively thick, for example more than 0.05 inch (0.125 cm.) thick. In another type of device the electrical connection to the PTC composition is made by an element composed of a conductive polymer which does not exhibit a useful T_s at any temperature below a useful T_s of the PTC composition. For further details of ways in which hotlines can be prevented reference should be made to the publications referred to above.

The invention also includes a heat-recoverable device which comprises a device as defined above in thermal contact with a heat-recoverable member of an organic polymer which will recover at a temperature below, preferably not more than 50°C. below, the useful T_s of the PTC composition (or the lowest useful T_s if there is more than one).

The invention also includes a heat-recoverable article which comprises a heat-recoverable member composed of a PTC composition as defined above and at least two electrodes which can be connected to a source of electrical power to cause current to flow through the PTC composition and thus heat the article to its recovery temperature. In this connection, a particularly useful discovery we have made is that by cross-linking a PTC composition in which the polymer is a thermoplastic crystalline polymer at a temperature above the melting point of the polymer, the tendency of the composition to lose its PTC character when stretched is greatly reduced.

The invention further includes a method of controlling the size of an electrical current flowing through an electrical circuit containing a PTC element by maintaining the temperature of the PTC element within a critical range thereof or by changing the temperature of the PTC element from a value outside a critical range thereof to a value inside that critical range (or *vice versa*), wherein the PTC element comprises a PTC composition as defined above. The temperature can be maintained or changed by the self-heating effect of the current passing through the element, or by external heating or cooling, or by a combination thereof.

Care is needed in the selection of the conductive filler, the polymer in which it is dispersed, and the cross-linking conditions, in order to ensure that a PTC composition having the desired characteristics is obtained. However, those skilled in the art will have no difficulty, having regard to the disclosure herein and their own knowledge, in making and using the invention and obtaining the advantages thereof.

Choice of Conductive Filler

We have found that conductive filler must have a particle size of at least 18 millimicrons, in order for a useful PTC effect to be obtained. As the particle size increases, the PTC behavior tends to become more pronounced. However, this valuable effect is counter balanced by the need to include greater proportions by weight of the larger-sized fillers to obtain the same resistivity. This does not put any very serious upper limit on the size of highly conductive fillers, e.g. metal particles, which may have sizes up to or even more than 1 micron. However, when using conductive carbon blacks, as is preferred, it is very difficult to achieve satisfactory

physical properties when using particle sizes greater than 100 millimicrons, because of the high proportions of carbon black needed to obtain the required resistivity. It is preferred that the carbon blacks used in this invention should have a maximum size of 80 millimicrons (average size when a mixture of carbon black is used).

As is well known in the art, carbon blacks are conventionally characterised by their particle size and by their nitrogen absorption and DBP (dibutyl phthalate) absorption values, which provide a measure of the porosity and aggregation of the primary particles. For details of these characteristics and their measurement, see for example "Analysis of Carbon Black", by Schubert, Ford and Lyon, in volume 8, at page 179, of Encyclopedia of Industrial Chemical Analysis (1969) published by John Wiley & Son, New York.

The preferred particle size of the carbon black is also dependent on the cross-linking temperature (T_c). As T_c increases, PTC behavior tends to become less pronounced, but this can be offset by an increase in the particle size of the carbon black. Thus it is preferred that the particle size should be at least 20 millimicrons when T_c is above 20°C, at least 30 millimicrons when T_c is above 100°C, and at least 40 millimicrons when T_c is above 150°C.

A large variety of carbon blacks are commercially available, but only a small proportion of them are known as conductive blacks and recommended for use in conductive polymer compositions. The preferred types of black for this invention are furnace and acetylene blacks, but the less conductive thermal and channel process blacks can also be used.

Examples of other conductive fillers, in addition to carbon black, are graphite, metal powders, conductive metal salts and oxides, and boron- or phosphorus-doped silicon or germanium.

The choice of a conductive filler will in addition be influenced by the polymer to be used, in particular the compatibility of the filler and polymer.

Choice of Polymer

As noted previously, the invention is useful with elastomers and thermoplastic polymers. The effect produced on a composition which already shows pronounced PTC behavior (e.g. one based on a crystalline polymer) will be relatively small, and generally will at most modify, and not remove an existing T_c , but will rather modify the characteristic around and above T_c and may even create a second PTC region having a second T_c . While such an effect is very valuable, we believe that the invention is even more useful when the cross-linked polymer is an elastomer, because of the variety of physical properties then available coupled with the ability to vary the T_c of the composition in a predictable way. The cross-linked polymer may be substantially free of carbon-carbon unsaturation, e.g. less than 5% molar concentration (C=C).

Suitable polymers in which the filler can be dispersed prior to cross-linking, and which are converted to elastomers by the cross-linking, include rubbers, elastomeric gums and thermoplastic elastomers. The terms "elastomeric gum", "gum" and "gum stock" are used herein to denote a polymer which is non-crystalline and has a glass transition temperature below T_c and preferably below room temperature (20°C), and which exhibits rubbery or elastomeric characteristics after being cross-linked. The term "thermoplastic elastomer" is used herein to denote a material which, even if not cross-linked, yet exhibits, in a certain temperature range, at least some elastomeric properties; such materials generally contain thermoplastic and elastomeric moieties. The filler can also be dispersed in a polymer which has been dynamically cross-linked, i.e. cross-linked while milling or otherwise shearing the polymer so as to obtain a product which can be subjected to further compound or forming processes.

We have found that the higher the green strength of the initial polymer, the more pronounced the PTC effect (other things being equal). On the other hand, as previously indicated, it may be desirable to anneal polymers having high green strength at or near T_c prior to cross-linking. Depending on the circumstances, therefore, it may be preferred to employ a polymer having low green strength, or a polymer having high green strength at 25°C. The term "polymer having high green strength" is well known in the art and denotes a polymer which exhibits a tensile stress of at least 10 psi at 20% elongation. Such polymers after being equilibrated at elevated temperature to the configuration favored at that temperature, will not change, or will change only very slowly, from this configuration, when cooled to room temperature. They also possess form stability at room temperature such that

articles prepared from them do not distort or flow to any significant extent, even though not cross-linked.

Suitable gums for use in the invention include polymers which contain carbon in the polymer backbone, as well as others, for example polyisoprene (both natural and synthetic), ethylene-propylene random copolymers, poly(isobutylene), styrene-butadiene random copolymer rubbers, styrene-acrylonitrile-butadiene terpolymer rubbers with and without added minor copolymerized amounts of α,β -unsaturated carboxylic acids, polyacrylate rubbers, polyurethane gums, random copolymers of vinylidene fluoride and, for example, hexafluoropropylene, polychloroprene, chlorinated polyethylene, chlorosulphonated polyethylene, polyethers, plasticized poly(vinyl chloride) containing more than 21% plasticizer, substantially non crystalline random co- or ter-polymers of ethylene with vinyl esters or acids and esters of α,β -unsaturated acids, and silicone gums and base polymers, for example poly(dimethyl siloxane), poly(methylphenyl siloxane) and poly(dimethyl vinyl siloxanes). The silicone gums and base polymers, which are particularly useful starting materials, have substantially no green strength.

Thermoplastic elastomers suitable for use in the invention, include graft and block copolymers such as:

(i) random copolymers of ethylene and propylene grafted with polyethylene or polypropylene side chains,

(ii) Block copolymers of α -olefins such as polyethylene or polypropylene with ethylene/propylene or ethylene/propylene/diene rubbers, polystyrene with polybutadiene, polystyrene with polyisoprene, polystyrene with ethylene-propylene rubber, poly(vinylcyclohexane) with ethylene-propylene rubber, poly(α -methylstyrene) with polysiloxanes, poly-carbonates with polysiloxanes, poly(tetramethylene terephthalate) with poly(tetramethylene oxide) and thermoplastic polyurethane rubbers.

Thermoplastic polymers suitable for use in the invention, which may be crystalline or non-crystalline, include:

(i) Polyolefins such as polyethylene, polypropylene.

(ii) Thermoplastic copolymers of olefins such as ethylene, propylene, with each other and with other monomers such as vinyl esters, acids or esters of α,β -unsaturated organic acids.

(iii) Halogenated vinyl or vinylidene polymers such as those derived from vinyl chloride, vinylidene chloride, vinyl fluoride, vinylidene fluoride and copolymers thereof with each other or with other halogenated or other unsaturated monomers.

(iv) Polyesters both aliphatic and partially or wholly aromatic such as poly(hexamethylene adipate or sebacate), poly(ethylene terephthalate) and poly(tetramethylene terephthalate).

(v) Polyamides such as Nylon-6, Nylon-6,6, Nylon-6,10 and "Versamids"*. (condensation products of dimerized and trimerized unsaturated fatty acids, in particular linoleic acid with polyamines).

(vi) Other materials such as polystyrene, polyacrylonitrile, thermoplastic silicone resins, thermoplastic polyethers, thermoplastic modified celluloses, and polysulphones.

Choice of cross-linking conditions

As noted previously, both T_c and the extent to which cross-linking is effected are extremely important in determining the resistance/temperature characteristics imparted to the composition. T_c not only plays a major role in determining T_c , but in addition the higher T_c , the less the degree of PTC exhibited (i.e. its slope and magnitude), other things being equal. Thus a carbon black/polymer combination which shows good PTC behavior due to the cross-linking when cross-linked at room temperature may show little or no PTC behavior due to the cross-linking when cross-linked at, for example, 170°C. The inhibiting effect of increasing T_c can often be counteracted by using a carbon black having a larger particle size and/or by increasing the level of cross-linking. We have found that it is essential that the cross-linked polymer have a gel fraction of at least 0.6, and often a higher gel fraction is necessary, e.g. at least 0.75. For most polymers the gel fraction should generally not exceed 0.96, but polysiloxanes and many unsaturated rubbers for example can be cross-linked to higher gel fractions without undesirably affecting the physical properties of the composition.

*Trade Mark

The crosslinks formed in the cross-linking operation should be stable in the temperature range in which the PTC composition is required to operate. Suitable covalent crosslinks include simple covalent bonds and cross-links comprising one or more of the linking structures

5 ---C---C--- , ---C---N--- , ---C---O--- , ---C---S---C--- , $\text{---C---SO}_2\text{---}$, ---Si--- ,
 ---C---CO--- , ---C---CO---O--- , ---CO---NR--- and ---CO---S--- .

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10 Ionic cross-links are also suitable provided that the composition exhibits form stability at least in the range in which PTC behavior is desired. Thus carboxylated elastomers partially or completely neutralized by sodium ion may be useful in the range up to 100°C. However, for most applications the more thermally form-stable compositions, which are partially or completely neutralized by di or polyvalent metal ions, are preferred.

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15 In considering the above discussion, those skilled in the art will readily understand that it is possible for polymer molecules to become linked together through mutual attachment to a third body for example, by chemical or strong physical bonding to the surface of the conductive filler, especially carbon black. Thus, the term cross-linking as used in this specification connotes any means of forming bonds between polymer molecules both directly or through the mediation of another small or large molecule or solid body provided only that such bonds result in coherency of the article and a degree of form stability throughout the operating or service temperature range of the composition.

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20 When covalent cross-linking is contemplated, there can be used any cross-linking process which will yield a product which has the required PTC characteristics and is form-stable in the range of utility. Thus cross-linking may be accomplished by irradiation or by chemical treatment. Suitable chemical cross-linking agents include, but are not limited to, organic peroxides and other precursor materials capable of yielding free radicals on the application of heat or other activation means, for example metal oxides and amines, or suitable reactive derivatives of amines; isocyanates and other compounds capable of reacting with groups containing active hydrogen to yield, for example ureas, urethanes, allophanates and the like; nitroso or oxide compounds such as *p*-quinone dioxine, and other difunctional chemicals containing at least one group capable of adding across double bonds such as organo-silane hydrides. Compounds containing sulfur which react with double bonds to yield mono sulfide bridged cross-links such as thiuram disulphide are also suitable. In many instances it may also be desired to add other materials to enhance the cross-linking effect such as, in the use of ionizing radiation or other free radical initiators, cross-linking coagents including, but not limited to, polyunsaturated compounds.

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25 30 35 40 45 50 55 60 Irradiation and peroxide cross-linking are preferred. Where ionizing radiation is used, doses between 5 and 50 mrads will generally achieve the desired cross-linking density without excessively compromising the physical properties of the product. Where peroxides are used, in general between 1 and 10 percent based on the polymer may be used. Part of the peroxide may be replaced by coagents. We have also discovered that when the cross-linked polymer is an elastomer, the degree of similarity between T_g and the cross-linking temperature (T_c) will depend on the thermal history of the composition prior to cross-linking. It is advantageous to maintain the composition at the cross-linking temperature for a brief period prior to subjecting said composition to the cross-linking process. For the majority of compositions the time required may be as short as one half minute, but for polymers possessing significant amounts of high molecular weight material (high Mooney viscosity gums), and which therefore have high green strength, a longer annealing period is preferred. Although we do not wish to be bound to any particular theory, the shortness of the annealing period indicates that the annealing serves to allow the polymer molecules to relax at their characteristic molecular relaxation rate into their preferred configurations at the cross-linking temperature. Thus T_g most nearly approaches T_c when the polymer molecules have been previously caused to assume an unstrained configuration at T_c prior to crosslinking.

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The aforesaid annealing is not related to the annealing of carbon black containing compositions which results in a diminution in the resistance of the composition, for example as described in Smith-Johannsen U.S. Patent No. 3,861,029, which process is believed to result in the "structuring" of the carbon black dispersion, i.e. the formation of preferred conductive pathways. Thus annealing for structuring takes much longer than the relaxation annealing referred

to hereinabove. We do find, however, that it is also advantageous to facilitate the structuring of the carbon black by annealing. When the desired cross-linking temperature is above about 170°C, it is often convenient to combine the two annealing steps and hold the composition in its final shaped form at T_c for a sufficient period of time to cause the desired structuring to occur prior to cross-linking the composition. Thus, a ten to twenty minute anneal at 200°C prior to cross-linking at that temperature is suitable. The time required for structuring is found to increase rapidly as the annealing temperature is decreased and for compositions which it is desired to cross-link at temperatures significantly below 200°C, it may be preferred to anneal at 200°C for a short period to reduce the resistance of the composition, optionally cool to room temperature and subsequently hold the composition at T_c for a sufficient time prior to crosslinking to relax the polymer molecules at T_c . Those skilled in the art will recognize that relaxation times for polymers vary widely with molecular weight and temperature (inter alia) and whilst in some circumstances compositions would relax almost instantaneously at T_c , in other circumstances a period of some minutes may be required to relax the molecules.

Moreover, it is possible by the use of plasticizers or other internal viscosity reduces to greatly reduce or even eliminate the relaxation anneal and in many circumstances to reduce the structuring anneal as well. Thus, the optional use of such plasticizers is contemplated in the instant invention. We prefer to use additives which can be polymerized or cross-linked into the polymer or which by some other means have their viscosity-reducing effect neutralized after the T_c anneal, since such additives can otherwise have a deleterious effect on the resistance stability of polymeric PTC heaters under service conditions. Plasticising additives are particularly useful when peroxide or any of the other thermally activated cross-linking processes are used, as it is not then possible conveniently to subject the composition to structural annealing. The peroxide or curing agents, when used, are often good viscosity reducers for the polymer, and other plasticizers may also be used to advantage.

The density of cross-linking, if above a certain minimum level, does not have a substantial effect on the T_c of the composition. However, the slope of the resistance temperature slope above T_c is a strong function of the cross-linking density; the higher said density the steeper the slope. Thus, the optimum cross-linking level is that which will achieve the desired resistance-temperature slope without undesirably compromising the physical properties of the product.

As briefly noted above, especially with polymer compositions which do not cross-link readily using ionizing radiation or chemical free radical generating additives such as peroxides, it is advantageous to add cross-linking promoters (or "coagents", to use a term known in the art). Such materials are usually unsaturated monomers. Suitable unsaturated monomers (or mixtures of monomers) generally contain at least two ethylenic double bonds in each molecule and preferably contain at least three. They should of course preferably be compatible with the polymer and have low volatility under the process conditions. Examples of such monomers include allyl esters of polycarboxylic acids and other acid moieties such as cyanuric acid, e.g., triallyl cyanurate and isocyanurate, diallyl aconitate, maleate and itaconate, and tetraallyl pyromellitate; bis and tris maleimides, e.g., N,N'-ethylene- and N,N' - *m* - phenylene - bis - maleimide; acrylic and methacrylic esters of polyhydric alcohols, e.g., dipentaerythritol hexamethacrylate, ethylene glycol dimethacrylate, 1,3-butylene glycol dimethacrylate and penta-erythritol tetramethacrylate; vinyl esters of polybasic acids, e.g. trivinyl cyanurate and citrate; vinyl and ether allyl ethers of polyhydric alcohols, e.g. the tetra-allyl and tetra-vinyl ethers of pentaerythritol; and bis acrylamides, e.g. N,N'-methylene- and N,N' - *p* - phenylene - bis - acrylamide. The amount of monomer required to provide a useful amount of cross-linking (as compared to a composition which is the same except for the presence of the monomer and has been processed in the same way) depends upon the particular monomer and the other ingredients, but can readily be determined by those skilled in the art having regard to the disclosure herein. Amounts within the range of 1 to 10% by weight of the composition, are generally satisfactory.

Other factors

As indicated above, the compositions of the invention may contain conventional ingredients such as antioxidants, flame retardants, inorganic fillers, thermal stabilisers, and processing aids. We have found that the presence of a non-

5 conductive filler (e.g. in amount 5 to 35% preferably 10 to 25%, based on the weight of the composition) is often advantageous. Particularly is this so when the polymer is a polysiloxane and the filler is silica. The presence of the non-conductive filler reduces the overall coefficient of expansion of the composition, and the improvement in PTC behavior is therefore surprising in view of the theory put forward by Kohler (see for example U.S. Patent No. 3,243,753) which attributes the PTC effect to the difference between the thermal expansion ratios of the conductive filler and the composition.

10 The invention is illustrated by the following Examples in which percentages are by weight and temperatures are in °C. The Examples are summarised in Table 3 below.

15 Except where otherwise stated, in each Example, the indicated polymer and carbon black were blended on a 4 inch (10 cm) two roll mill to give a blend containing the indicated percentage of carbon black, and the blend pressed into a sheet 6x6x0.03 inch (15x15x0.075 cm.). Strips 1.5x1x0.03 inch (3.8x2.5x0.075 cm.) were cut from the sheet. Electrodes were created on opposite ends and opposite faces of the long dimension of each strip by painting thereon 0.25 inch (0.64 cm.) wide bands of silver paint. The strip was annealed for 10 minutes at 200°C. It was then placed on a metal plate maintained at the indicated temperature (± 10°C) and (when the plate temperature was greater than room temperature) was allowed to equilibrate with the plate, giving the polymer time to relax. The strip was then cross-linked, while maintaining the plate at the indicated temperature, by exposure to the indicated irradiation dose in Megarads from a 6 mA beam of about 0.7MV electrons; the strip was thereby heated to a somewhat higher temperature, usually 10 to 20°C higher at the higher dose. After cooling, the strip was heated slowly from room temperature to its peak temperature, measuring its resistance between the electrodes at 15°C intervals. The resistances in the steepest portion of the resistance/temperature curve were fitted to an expression of the form

$$\ln(R_t/R_0) = \alpha(T - T_0)$$

30 (where R_t was the resistance at Temperature T and R_0 was the resistance at the temperature T_0 at the start of this portion of the curve), and α was calculated. For a curve having an R_{14} greater than 2.5 and an R_{30} greater than 6, α is at least about 0.06.

35 Details of the carbon blacks used in the Examples are given in Table 1 below. Details of the polymers used in the Examples are given in Table 2 below. Details of the Examples themselves are given in Table 3, which also gives the significant resistance/temperature characteristics of the products.

40 In Table 3, the polymers and carbon blacks are identified by their numbers as set out in Tables 1 and 2; the trade names of the polymers are also given and for the carbon blacks the particle size, nitrogen absorption and dibutyl phthalate absorption values are given in parentheses after the identification number. The reference numerals of Comparative Examples not in accordance with the invention are marked with an asterisk (*).

TABLE I
Carbon Blacks

Type No.	Trade Name	Industry Class	ASTM D1976—67 Class	Size Mu	N ₂ m ^{2/g}	DBP cc/100 g
1.	Black Pearls* 900		N1	15	230	65
2.	Black Pearls 880		N1	16	220	110
3.	Regal* 660			17	112	54
4.	Black Pearls 700		N1	18	200	122
5.	Vulcan* 9H	SAF-HS	N166	11—19	142	135
6.	Vulcan 9	SAF	N110	19—21	140	114
7.	Vulcan SC	SCF	N294	22	203	106
8.	Vulcan 5H		N285	24	100	126
9.	Regal 330			25	94	70
10.	Regal 330R			25	94	62
11.	Vulcan C	CF	N293	20—25	145	100
12.	Elftex* 8			27	85	103
13.	Vulcan M		N339	28	92	121
14.	Ketjen* Black EC	EC		30	1000	340
15.	Vulcan XC-72	XCF	N472	30	254	178
16.	Vulcan 3H	HAF-HS	N347	26—30	90	124
17.	Regal 99	FF	N440	36	46	60
18.	Sterling* S0	FEF	N550	42	42	120
19.	Sterling S0—1	FEF-LS	N539	42	42	109
20.	Sterling N765	SRF-NS	N765	60	30	116
21.	Regal SRF-S	SRF-NS		60	30	64
22.	Sterling NS	SRF-HM-NS	N774	75	27	70

TABLE 2
Polymers

Type No.	Trade Name	Polymer Type	Filler Type	
30	1. Silastic* 35U	Polydimethyl siloxane containing vinyl groups (0.4%)	Silica	30
	2. SE 76	Polydimethyl siloxane free from vinyl groups	None	
35	3. Silastic 55U	Polydimethyl siloxane containing vinyl groups (0.4%)	Silica, in greater quantity than Silastic 35U	35
	4. Silastic 410	Polydimethyl siloxane having a high vinyl content (4%)	None	
40	5. Silastic 437	Polydimethyl siloxane containing vinyl groups (0.4%)	Silica	40
	6. Viton* B50	Vinylidene difluoride copolymer	None	
45	7. Nordan* 1470	Ethylene/propylene/diene terpolymer	None	45
	8. Epsyn 5508	Ethylene/propylene/diene terpolymer with high green strength	None	
50	9. TPR 2000	An ethylene/propylene rubber which contains about 20% polypropylene and has been lightly cross-linked under dynamic conditions so that it is a thermoplastic elastomer	None	50
	10. Nysin 35-8	An acrylonitrile/butadiene rubber containing 35% acrylonitrile	None	
55				55
60	11. Natsyn* 220	A cis-1,4-polyisoprene	None	
	12. DYNH	A low density polyethylene	None	60

*Trade marks

TABLE 3

Examples	Polymer 1. Silastic 35U	Carbon Type 14. (30/1000/340)	Black %	Radiation Dose	Curing Temp. C 25	Resistance (Megohms) at 25°C 0.8	T _g 23-45	T _o - - - 190	Peak Temp. - - - - 190	R ₁₀₀ >10 >10 10 >10	R ₂₀₀ 4.0 5.2 2.3 2.3 6.1	R ₄₀₀ 2.0 0.058 0.018 0.065 0.065
1.			5	20	"	-	-	-	-	0.048	2.0	
2.			5	50	"	2.0	-	-	-	0.058	2.3	
3.			8	20	"	0.01	-	-	-	0.018	1.3	
4.			8	50	"	0.01	>20	>250	>250	0.065	2.5	
5.	"	16. (26-30/90/ 124)	30	10	"	0.01	-	-	-	0.053	2.1	4.5
6.	"	7. (22/203/106)	25	20	"	0.03	>20	>110	>110	0.096	3.8	13.3
7.	"	12. (27/85/103)	25	10	"	0.007	>20	>170	>170	0.077	2.9	9.0
8*	"	10. (42/42/109)	25	20	"	0.02	>20	>115	>115	0.134	6.5	34.4
9.		11. (25/94/62)	50	50	"	0.1	>20	>90	>90	0.125	5.8	27.5
10.	"	12. (42/42/109)	35	10	"	0.002	>20	>280	>280	0.051	2.0	4.3
11.		13. (25/94/70)	25	10	"	0.005	>10	>190	>190	0.091	3.6	11.6
12.		14. (42/42/109)	40	40	"	0.01	>20	>90	>90	0.132	6.4	32.8
13.	"	15. (25/94/62)	90	90	"	0.01	>20	>75	>75	0.173	11.2	90.0
14.		16. (25/94/70)	5	10	"	0.001	-	>100	>235	0.057	2.2	1.7
15.		17. (25/94/62)	25	20	"	0.002	>20	>220	>220	0.11	4.6	19.9
16.		18. (25/94/62)	50	50	"	0.007	>20	>100	>100	0.08	3.1	8.8
17.*	"	19. (25/94/62)	25	10	"	0.03	>20	>100	>100	0.07	2.7	7.0
18.		20. (25/94/62)	50	50	"	0.1	>20	>130	>130	0.082	3.2	9.4
19.		21. (25/94/62)	35	20	"	0.01	>20	>110	>110	0.112	4.8	19.8
20.		22. (25/94/62)	50	50	"	0.05	>20	>100	>100	0.112	4.8	19.8
21.	"	23. (25/94/62)	25	10	"	0.01	>20	>110	>110	0.112	4.8	19.8
22.		24. (36/46/60)	45	45	"	0.01	>20	>100	>100	0.112	4.8	19.8
23.		25. (60/30/64)	20	50	"	0.05	>20	>100	>100	0.112	4.8	19.8
24.		26. (60/30/64)	50	50	"	0.01	>20	>100	>100	0.112	4.8	19.8
25.		27. (60/30/64)	25	20	"	0.05	>20	>100	>100	0.112	4.8	19.8
26.		28. (60/30/64)	50	50	"	0.01	>20	>100	>100	0.112	4.8	19.8
27.		29. (60/30/64)	40	5	"	0.004	>20	>100	>100	0.112	4.8	19.8
28.		30. (60/30/64)	10	10	"	0.004	>20	>100	>100	0.112	4.8	19.8
29.	1. Silastic 35U	20. (60/30/64)	50	50	"	0.004	>20	>100	>100	0.112	4.8	19.8
30.		31. (60/30/64)	25	20	"	0.004	>20	>100	>100	0.112	4.8	19.8
31.		32. (60/30/64)	50	50	"	0.006	>20	>100	>100	0.115	5.0	21.5
32.		33.* (20-25/145/ 100)	25	30	"	0.07	>20	>100	>100	0.03	1.5	2.1
33.		34. (21/40/114)	25	50	"	0.2	>20	>100	>100	0.07	2.8	6.1
34.		35. (21/40/114)	20	50	"	0.03	>20	>100	>100	0.03	1.6	2.7
35.		36. (21/40/114)	50	50	"	0.3	>20	>100	>100	0.065	2.5	6.0

TABLE 3 (cont.)

Example	Polymer	Carbon Black Type	%	Radiation Dose	Curing Temp. °C	Resistance (Megohms) at 25°C at Peak	T _g	T ₀	Peak Temp.	α	R ₁₄	R ₃₀	R ₁₀₀
37.	"	8. (24/100/126)	30	20	"	0.005	>20	"	>115	0.039	1.7	3.2	>10 >100
38.	"	13. (28/92/121)	30	20	"	0.005	>20	"	>140	0.087	3.4	10.6	>10 >100
39.	"	22. (75/27/70)	42	5	"	0.02	4	"	>140	0.040	1.8	3.3	>10 >100
40.	"	42. (75/27/70)	42	10	"	0.03	>20	"	>190	0.082	3.2	9.3	>10 >100
41.	"	43. (30/254/178)	20	20	"	0.04	>20	"	>100	0.097	3.9	13.6	>100
42.	"	44. (30/254/178)	50	50	"	0.1	>20	"	>100	0.097	3.9	13.4	>100
43.	"	45. (30/254/178)	20	20	"	0.02	>20	"	>85	0.048	1.9	3.9	>10 >10
44.	"	46. (11-19/142/ 135)	50	50	"	0.007	>20	"	>40	0.070	2.6	6.8	>10 >10
45.	"	47.* (11-19/142/ 135)	20	50	"	0.002	>20	"	>40	0.017	1.3	1.8	<10 <0
46.	"	48.* (11-19/142/ 135)	25	50	"	0.001	>20	"	>40	0.045	1.9	3.7	<10 <0
47.*	"	49.* (17/112/54)	25	50	"	0.001	>20	"	>40	0.027	1.5	2.4	<10
50*	"	50.* (16/220/110)	24	50	"	0.02	>20	"	>40	0.019	1.3	1.9	<10
51.*	"	51.* (15/230/65)	30	50	"	0.0006	>20	"	>40	0.007	1.1	1.4	<10
52.*	2. SE-76	52.* (30/100/340)	14.	8	5	25	>20	"	>40	<0	<1	<1	<10 <10
53.*	"	53.* (75/27/70)	45	10	"	25	>20	"	>40	0.01	1.2	1.6	<10 >100
54.*	"	54.* (75/27/70)	45	20	"	25	>20	"	>40	0.058	2.3	5.1	<10 >100
55.	"	55. (25/94/70)	40	40	"	25	>20	"	>40	0.086	3.4	10.4	<10 >100
56.	"	56. (25/94/70)	25	5	"	25	>20	"	>40	0.018	1.3	1.9	<10 >100
57.*	"	57.* (25/94/70)	10	10	"	25	>20	"	>40	0.103	4.2	15.6	>100 >100
58.	"	58. (25/94/70)	20	20	"	25	>20	"	>40	0.1	13.1	13.1	>100 >100
59.	"	59. (25/94/70)	20	20	"	25	>20	"	>40	<0	—	—	>100 >100
60.*	"	60.* (25/74/62)	10	10	"	25	>20	"	>40	<0	—	—	>100 >100
61.*	"	61.* (30/254/178)	15	10	"	25	>20	"	>40	<0	—	—	>100 >100
62.*	"	62.* (30/254/178)	20	20	"	25	>20	"	>40	0	—	—	>100 >100

TABLE 3 (cont.)

Examples	Polymer	Carbon Black Type	Black %	Radiation Dose	Curing Temp. °C	Resistance (Megohms) at 25°C at Peak	T. Constant from 25 to 175°C	T. 175°C	R ₁₀₀
63.*	1. Silastics 35U	4. (18/200/122)	20	12	"	0.0012	(11 at 145°C)	-40	>100
64.*	3. Silastics 55U	4. (18/200/122)	20	12	"	0.0011	(11 at 130°C)	-40	>100
65.	4. Silastic 410	18. (42/42/120)	35	18	"	0.0012	(11 at 145°C)	-40	70 >190
66.	5. Silastic 437	18. (42/42/120)	35	18	"	0.0011	(11 at 145°C)	-40	120 >200
67.	5. Silastic 437	15. (30/254/178)	20	9	25	0.0016	25-40	130 >220	29 7
68.	6. Viton B50 containing 2% triallyl isocyanurate	15. (30/254/178) containing 2% CaO	15	20	25	0.0025	15	145 >220	0.065 2.5
69.	7. Viton B50 containing 2% triallyl isocyanurate	18. (42/42/120)	25	20	110	0.0028	0.4	175 >220	0.060 2.5
70.*	8. Propane trimethacrylate	18. (42/42/120)	35	9	25	0.0028	-0.02	-170 >220	0.04 1.7
71.	9. Silastic 437	18. (42/42/120)	35	9	25	0.0028	-0.006	-190 >220	0.01 1.2
72.	10. Propane trimethacrylate	18. (42/42/120)	35	9	25	0.0028	-1.5	-50 >170	0.13 6.2
73.	11. Propane trimethacrylate	18. (42/42/120)	35	9	25	0.0015	0.02	-130 >250	0.054 2.1
74.	12. Propane trimethacrylate	18. (42/42/120)	35	9	25	0.0012	-	-165 >250	- 2
75.	13. Propane trimethacrylate	18. (42/42/120)	35	9	25	4x10 ⁻³	4x10 ⁻⁶	70 280	0.05 2.0
76.	14. Propane trimethacrylate	18. (42/42/120)	35	9	25	0.0007	2	-25 280	0.046 1.9
77.	15. Propane trimethacrylate	18. (42/42/120)	35	9	25	0.0006	5	-110 280	0.073 2.8
78.	16. Propane trimethacrylate	18. (42/42/120)	35	9	25	0.0005	-0.1	-150 280	0.051 2.0
79.	17. Propane trimethacrylate	18. (42/42/120)	35	9	25	0.0004	-0.01	-195 280	0.037 1.7
80.	18. Propane trimethacrylate	18. (42/42/120)	35	9	25	0.0008	-2	-25 280	0.084 3.3
81.	19. Propane trimethacrylate	18. (42/42/120)	35	9	25	0.0003	>20	-110 280	0.096 3.8
82.	20. Propane trimethacrylate	18. (42/42/120)	35	9	25	0.0002	>2	-150 280	0.094 3.7
83.	21. Propane trimethacrylate	18. (42/42/120)	35	9	25	0.0001	>0.2	200 280	0.069 2.6
84.	22. Propane trimethacrylate	18. (42/42/120)	35	9	25	0.001	>20	100 280	0.11 7.5
85.	23. Propane trimethacrylate	18. (42/42/120)	35	9	25	0.0003	>20	175 280	0.154 8.6
86.	24. Propane trimethacrylate	18. (42/42/120)	35	9	25	0.0001	>20	160 220	0.146 7.7
87.	25. Propane trimethacrylate	18. (42/42/120)	35	9	25	0.0001	>0.2	205 220	0.077 2.9
88.	26. SE-76	18. (42/42/120)	35	40	25	0.008	>1000	130 220	-0.2 -18.0
89.	27. SE-76	18. (42/42/120)	35	40	25	0.0015	0.5	100 280	0.07 2.6
90.	28. SE-76	18. (42/42/120)	35	40	25	0.0009	0.1	160 280	0.046 1.9
91.	29. SE-76	18. (42/42/120)	35	40	25	0.0002	-	225 235	0.0045 1.9

TABLE 3 (cont.)

Example	Polymer	Carbon Black Type	%	Radiation Dose	Curing Temp. °C	Resistance (Megohms) at 25°C at Peak	T _g	Peak Temp.	α	R ₃₀	R ₁₀₀	
92.	7. Nordel	18. (42/42/120)	30	20	25	0.005 >1140	40	70	-160	0.23	25 >1000	
93.						0.0002 100	105	115	-220	0.15	7.7 >100	
94.						0.0001 140	110	110	-220	0.086	3.3 >100	
95.	8. Epsyn	18. (42/42/120)	48	10	25	0.0004 >10	110 -160	175	>250	0.070	2.8 >100	
96.	5508					0.0004 >10	150	150	-200	0.089	3.5 >1000	
97.						0.0001 100	160	160	-200	0.12	5.4 >1000	
98.						0.0002 40	110	250	0.09	3.5	10 >100	
99.	8. Epsyn	18. (42/42/120)	45	20	15	0.0002 >1000	130 -140	160 150	240 >200	0.11 0.167	4.5 10.4 >100 >1000	
100.	5508		40	See note	185	0.065 0.1	>10 >1000	-150	175 >200	0.085 0.167	1.5 1.50 >100 >1000	
101.	8. Epsyn 5508	18. (42/42/120)	27	See note	185	0.065 0.09	>10 185 & 25	-150 -130	175 >200	0.085 0.015	3.3 8 >100 >1000	
102.	5. Silastic (39.3% and 437 (33.7%)											
103.	5. Silastic	18. (42/42/120)	35	See note	200	-0.0007 200 & 25	>10 160 160 25	-205 -195 >10 -110	220 220 >250 175 >250	0.085 0.085 3.3 0.092	3.3 3.3 1.6 3.6 >100 >100	
104.	437											
105.												
106.												
107.	5. Silastic	18. (42/42/120)	45	18	25	0.005 >10		25-45	40	-0.1	-4 >1000	
108.	9. TPR 2000	15. (30/254/178)	30	12	180	0.001 >0.01		-170	170	>240	- >10	
109.	10. Nysin 35-8	15. (30/254/178)	30	20	25	0.01 0.002 0.001	-10 -0.035 0.007	25-40 150 180	70 175 205	145 235 250	0.09 0.06 0.046	3.5 2.5 1.9 >100 17 <10
110.												
111.												
112.	11. Natsyn 2200	18. (42/42/120)	40	20	25	0.15 0.017 0.010 0.012 0.001	40 2 2 0.2 0.03	-25 -110 150 -175 70 & 170	55 145 175 175 80 & 165	130 190 220 210 220	0.065 0.083 0.083 0.054 —	2.5 3.2 3.2 2.1 — >100 60 -100 5 12 >10 & 8 — >10 & 15 — >15 & 6 —
113.	with 0.05% antioxidant											
114.												
115.												
116.	12. DYNH	15. (30/254/178)	20	12	150	0.001 0.001 0.003 0.009	0.1 0.1 0.1 0.09	70 & 160 75 & 150 100 & 170 75 & 185	80 & 160 75 & 150 100 & 170 100 & 195	215 — — —	— — — —	
117.			20	See note								
118.	12. DYNH	15. 18.	20									
119.												

Examples 92-94

The Nordel-containing compositions were prepared in a Banbury mixer. Both the Nordel- and Epsyn-containing compositions were annealed at 200°C for 5 minutes after they had been irradiated. The resistance of the second Nordel-containing composition, which had been irradiated at 100°C, decreased from 25 to 100°C.

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Examples 97 and 98

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Example 97 was irradiated within a few minutes of being placed on the hot plate and had a very indefinite T_g in the range from 30-100°C. Example 98 was allowed to equilibrate and relax longer before irradiation and had a more clearly marked T_g at 100°C. Furthermore, the resistance of 98 was relatively constant from 40° to T_g while that of 97 doubled in the 30° range from 25 to 70°C.

Examples 100, 101, and 102

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The curable compositions also contained 2,5 - dimethyl - 2,5 - di - (t - butylperoxy)hexane (about 4.9% in Example 100 and about 4% in Examples 101 and 102) and an antioxidant (about 1% in Example 100 and about 0.5% in Examples 101 and 102). In Examples 100 and 101 the compositions were cured without irradiation by placing them for 20 minutes in a hydraulic press at 185°C. In Example 102 the composition was first cured in this way and then irradiated at 25°C to a dosage of 12 Mrads. The resistance of the sample in Example 100 remained at about 0.1 megohm up to about 115°C and then began to rise. The resistance of the sample in Example 101 dropped from about 0.065 Megohms at 25°C to about 0.033 megohms at 85°C and then began to rise. The resistance of the sample in Example 102 remained at about 0.09 megohms up to about 110°C and then began to rise.

Examples 103 and 104

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The curable composition also contained about 2% of 2,5 - dimethyl - 2,5 - di - (t - butylperoxy)hexyne - 3. (Trade Mark—Luperco 130XL). In Example 103, the composition was cured by heating to 200°C. In Example 104, the composition was cured by heating to 200°C, followed by irradiation at 25°C to a dosage of 5 Mrads. The effect of the irradiation is to increase the (comparatively low) rate at which the resistance increases at temperatures below T_g .

Examples 105 and 106

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The curable composition also contained about 2% of dicumyl peroxide (40% active) (Trade Mark—Di-Cup). In Example 105 the composition was cured by heating at 160°C. In Example 106, the composition was cured by heating at 160°C followed by irradiation at 25°C to a dosage of 5 Mrads. The effect of irradiation is much more marked than in Example 104 and is greatly to increase the rate at which the resistance increases at temperatures below T_g , which becomes much more difficult to discern.

Example 108

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The resistance/temperature curve of this Example showed no trace of the resistance peak at 155°C which is seen when the same composition is irradiated to 12 Mrads at room temperature and which is associated with the melting of the polypropylene.

Similar results to those shown in the preceding Examples have been obtained with the following cross-linked polymers: chlorinated polyethylene, polyethyl acrylate chlorosulphonate polyethylene, plasticized and polyvinyl chloride.

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In the accompanying drawings, in which the words "Silastic", "Vulcan", "Luperco" and "Di-Cup" are trade marks, Figure 1 shows the resistance/temperature characteristics of the strips produced in Examples 67 to 70; Figure 2 shows the resistance/temperature characteristics of the strips produced in Examples 103 and 104; and Figure 3 shows the resistance/temperature characteristics of the strips produced in Example 105, 106 and 107.

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Examples 118 and 119

The curable compositions also contained about 1% of an antioxidant (Age-rite Resin D), about 2% of peroxide, and in Example 118 only about 2% of triallylisocyanurate.

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In U.S. Patent No. 3,757,088, there is disclosed a process in which an epihalohydrin rubber, carbon black, and a chemical curing agent are mixed, and

the resulting composition is cured by heating, without annealing, between the mixing temperature and the curing temperature.

In Japanese Patent Applications Nos. 51-39742 and 51-39743, processes are described in which an ethylene-propylène rubber, an ethylene-propylene terpolymer rubber, a butyl rubber, or a halogenated butyl rubber, is mixed with a carbon black having a particle size within the range of from 50 to 250 μ and a chemical cross-linking agent, and the resulting composition is cured by heating without annealing between the mixing temperature and the curing temperature.

None of these documents describes the effects obtained by the present applicants.

No claim is made herein to a process in which an epihalohydrin rubber, carbon black, and a chemical curing agent are mixed, and the resulting composition is cured by heating, without annealing between the mixing temperature and the curing temperature, or to the product of such a process.

No claim is made herein to a process in which an ethylene-propylene rubber, an ethylene-propylene terpolymer rubber, a butyl rubber, or a halogenated butyl rubber, is mixed with a carbon black having a particle size within the range of from 50 to 250 μ and a chemical cross-linking agent, and the resulting composition is cured by heating without annealing between the mixing temperature and the curing temperature, or to the product of any such process.

Subject to the foregoing disclaimers,

WHAT WE CLAIM IS:—

1. A composition comprising:

(1) a cross-linked polymer; and

(2) conductive particles enclosed within the cross-linked network of said polymer, the particles having a size of at least 18 millimicrons; the polymer of which composition has a gel fraction of at least 0.6, and which composition has at least one useful T_g (as hereinbefore defined), subject to the proviso that, when the polymer comprises a cross-linked crystalline polymer and the composition had a useful T_g prior to cross-linking, the cross-linked composition has at least two useful T_g values.

2. A composition according to Claim 1 which has at least one useful T_g between 25° and 200°C.

3. A composition according to Claim 1 or 2 which has a resistivity of at least 25 ohm cm at the higher of 25°C and a temperature 50°C below the useful T_g or the lowest useful T_g if the composition has more than one useful T_g .

4. A composition according to any one of the preceding Claims which has a resistivity at 25°C of at least 3 ohm cm.

5. A composition according to Claim 4 which has a resistivity of at least 25 ohm cm.

6. A composition according to any one of the preceding claims which has at least one critical range (as hereinbefore defined) having an R_{30} value (as hereinbefore defined) of at least 6.

7. A composition according to any one of the preceding Claims which has more than one useful T_g .

8. A composition according to any one of the preceding Claims which has a Peak Ratio (as hereinbefore defined) of at least 20:1.

9. A composition according to Claim 8 which has a Peak Ratio of at least 100:1.

10. A composition according to any one of the preceding Claims which has a useful T_g below 150°C and in which the ratio of the resistivity at 200°C to the resistivity at the useful T_g is at least 20:1.

11. A composition according to any one of Claims 1 to 9 which has a useful T_g above 150°C and in which the ratio of the resistivity at 250°C to the resistivity at the useful T_g is at least 20:1.

12. A composition according to any one of the preceding Claims in which the or each useful T_g remains substantially unchanged when the composition is repeatedly subjected to thermal cycling which comprises heating the composition from a temperature below the useful T_g to a temperature above the useful T_g but below the peak temperature (as hereinbefore defined), followed by cooling to a temperature below the useful T_g .

13. A composition according to any one of the preceding Claims wherein the conductive particles are carbon black particles having an average size of 22 to 80 millimicrons.

14. A composition according to any one of the preceding Claims wherein the polymer is an elastomer. 5

15. A composition according to Claim 14 wherein the elastomer contains carbon in the polymer backbone. 5

16. A composition according to Claim 14 wherein the polymer is a polysiloxane. 5

17. A composition according to any one of Claims 1 to 13 wherein the polymer is a thermoplastic crystalline polymer. 10

18. A composition according to any one of the preceding Claims which also contains non-conductive particles enclosed within the cross-linked network of the polymer. 10

19. A composition according to Claim 17 wherein the polymer is a polysiloxane and the non-conductive filler is silica. 15

20. A composition according to any one of the preceding Claims wherein the polymer is cross-linked by covalent cross-links selected from the structures 15

—C—C—, —C—N—, —C—O—, —C—S—C—, —C—SO₂—, —Si—,
—C—CO—, —C—CO—O—, —CONR— and —CO—S—.

21. A composition substantially as described in any one of the foregoing examples. 20

22. A process for the preparation of a composition as claimed in any one of the preceding Claims, which process comprises: 20

(1) dispersing conductive particles having a size of at least 18 millimicrons in a polymer;

(2) cross-linking the dispersion from step (1) to obtain a composition of which the polymer has a gel fraction of at least 0.6 and which composition comprises conductive particles enclosed within the cross-linked network of the polymer; 25

the particles, the polymer, and the cross-linking conditions being such that the cross-linked composition has at least one useful T_g, subject to the proviso that when the polymer comprises a crystalline polymer and the composition has a useful T_g prior to cross-linking, the cross-linking is effected in two stages carried out at substantially different temperatures or is effected under conditions such that the cross-linked composition has a useful T_g above the useful T_g of the composition before cross-linking. 30

23. A process according to Claim 22 wherein the polymer is an elastomer gum. 35

24. A process according to Claim 22 or 23 wherein the polymer used in step (1) is one which has been dynamically cross-linked.

25. A process according to any one of Claims 22 to 24 wherein the polymer has a tensile stress of at least 10 psi at 20% elongation. 40

26. A process according to any one of Claims 22 to 24 wherein the polymer has a tensile stress of less than 10 psi at 20% elongation. 40

27. A process according to any one of Claims 22 to 26 wherein the polymer is annealed at the cross-linking temperature prior to cross-linking.

28. A process according to Claim 22 wherein the polymer comprises a crystalline polymer and the composition has a useful T_g prior to cross-linking, and the composition is cross-linked at a temperature above the peak of the crystalline melting range. 45

29. A process according to any one of Claims 22 to 28 wherein the polymer is cross-linked by irradiation.

30. A process according to any one of Claims 22 to 28 wherein the polymer is cross-linked with the aid of a chemical cross-linking agent. 50

31. A process according to any one of Claims 22 to 30 wherein the cross-linking temperature is above 20°C and the conductive filler is a carbon black having a particle size of at least 20 millimicrons. 55

32. A process according to any one of Claims 22 to 30 wherein the cross-linking temperature is above 100°C and the conductive filler is a carbon black having a particle size of at least 30 millimicrons.

33. A process according to any one of Claims 22 to 30 wherein the cross-linking temperature is above 150°C and the conductive filler is a carbon black having a particle size of at least 40 millimicrons. 60

34. A process according to any one of Claims 22 to 33 wherein the dispersion

from step (1) is cross-linked at a first temperature (T_{c1}) and then at a second temperature (T_{c2}) which is substantially different from T_{c1} .

35. A process according to Claim 34 wherein the polymer is a thermoplastic and T_{c1} is substantially lower than T_{c2} .

36. A process according to Claim 35 wherein the polymer is an elastomer gum and T_{c1} is substantially higher than T_{c2} .

37. A process according to any one of Claims 33 to 36 wherein the polymer is annealed at each cross-linking temperature prior to cross-linking.

38. A process according to Claim 22 substantially as hereinbefore described.

39. A process according to Claim 22 substantially as described in any one of the foregoing examples.

40. A composition according to any one of Claims 1 to 21 when prepared by a process as claimed in any one of Claims 22 to 39.

41. A device comprising a PTC element (as herein before defined) and at least two electrodes which can be connected to a source of electrical power to cause current to flow through the PTC element wherein the PTC element comprises a composition as claimed in any one of Claims 1 to 21 and 40.

42. A device according to Claim 41 which is so constructed and arranged that when the electrodes are connected to a source of electrical power, the current flows through the PTC element in a way which substantially avoids the formation of hot lines.

43. A device according to Claim 41 or 42 which is a strip heater.

44. A device according to Claim 42 which comprises two parallel electrodes which are separated by a distance d and are enclosed within a web of the composition, the portion of the web between the electrodes having a minimum thickness t which is greater than the maximum dimension of the electrodes in the same dimension and is such that d/t is less than 7.

45. A device according to Claim 44 wherein d/t is less than 5.

46. A device according to Claim 45 wherein d/t is 3 to 4.

47. A device according to Claim 42 wherein the composition is in the form of a layer and the electrical connections thereto are such that the current flows predominantly through the thickness of the layer when it is at T_s .

48. A device according to Claim 47 wherein at least one of the electrical connections to the composition is made through a layer of a conductive polymer which does not exhibit a useful T_s at any temperature below a useful T_s of the composition.

49. A heat-recoverable device which comprises a device as claimed in any one of Claims 41 to 48 in thermal contact with a heat-recoverable member which will recover at a temperature below the useful T_s of the composition.

50. A device according to Claim 49 wherein the heat-recoverable member is composed of an organic polymer.

51. A heat-recoverable article which comprises a heat-recoverable member composed of a composition as claimed in any of Claims 1 to 21 and 40.

52. An article according to Claim 51 wherein the polymer in the PTC composition consists of a thermoplastic crystalline polymer and the composition has been cross-linked at a temperature above the melting point of the polymer.

53. A method of controlling the size of an electrical current flowing through an electrical circuit containing a PTC element by maintaining a PTC element at a temperature within a critical range thereof or by changing the temperature of the PTC element from a value outside a critical range thereof to a value inside that critical range, or vice versa, wherein the PTC element comprises a composition as claimed in any one of Claims 1 to 21 and 40.

54. A composition comprising:

- (1) a cross-linked polymer; and
- (2) conductive particles enclosed within the cross-linked network of said polymer, the particles having a size of at least 18 millimicrons;

the polymer of which composition has a gel fraction of at least 0.6, and which composition has at least one useful T_s (as hereinbefore defined), subject to the proviso that, when the polymer comprises a cross-linked crystalline polymer and the composition had a useful T_s prior to cross-linking, the cross-linked composition has at least two useful T_s values, and subject to the proviso that the composition is other than (a) a chemically cross-linked composition comprising an ethylene-propylene rubber, ethylene-propylene terpolymer rubber, a butyl rubber, or a halogenated butyl rubber, in admixture with carbon black having a particle size within the range

of from 50 to 250 μ , or (b) a chemically cross-linked composition comprising epihalohydrin rubber.

55. A process for the preparation of a composition as claimed in claim 54 which process comprises:

- 5 (1) dispersing conductive particles having a size of at least 18 millimicrons in a polymer;
- 10 (2) cross-linking the dispersion from step (1) to obtain a composition of which the polymer has a gel fraction of at least 0.6 and which composition comprises conductive particles enclosed within the cross-linked network of the polymer;
- 15 the particles, the polymer, and the cross-linking conditions being such that the cross-linked composition has at least one useful T_g , subject to the proviso that when the polymer comprises a crystalline polymer and the composition has a useful T_g prior to cross-linking, the cross-linking is effected in two stages carried out at substantially different temperatures or is effected under conditions such that the cross-linked composition has a useful T_g above the useful T_g of the composition before cross-linking, and subject to the proviso that the resulting composition is other than (a) a chemically cross-linked composition comprising an ethylene-propylene rubber, ethylene-propylene terpolymer rubber, a butyl rubber, or a halogenated butyl rubber, in admixture with carbon black having a particle size within the range of from 50 to 250 μ , or (b) a chemically cross-linked composition comprising epihalohydrin rubber.
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56. A device comprising a PTC element (as hereinbefore defined) and at least two electrodes which can be connected to a source of electrical power to cause current to flow through the PTC element wherein the PTC element comprises a composition as claimed in Claim 54.

57. A heat-recoverable article which comprises a heat-recoverable member composed of a composition as claimed in Claim 54.

58. An article according to Claim 57 wherein the polymer in the composition consists of a thermoplastic crystalline polymer and the composition has been cross-linked at a temperature above the melting point of the polymer.

59. A method of controlling the size of an electrical current flowing through an electrical circuit containing a PTC element by maintaining the PTC element at a temperature within a critical range thereof or by changing the temperature of the PTC element from a value outside a critical range thereof to a value inside that critical range, or *vice versa*, wherein the PTC element comprises a composition as claimed in Claim 54.

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3 SHEETS This drawing is a reproduction of
 the Original on a reduced scale
 Sheet 1

PASSIVE RESISTANCE OF $1\frac{1}{2}$ " x 1" SLABS
(THICKNESS 0.030" SILVER PAINT ELECTRODES $\frac{1}{4}$ " WIDE,
1" APART)

2919-48-3

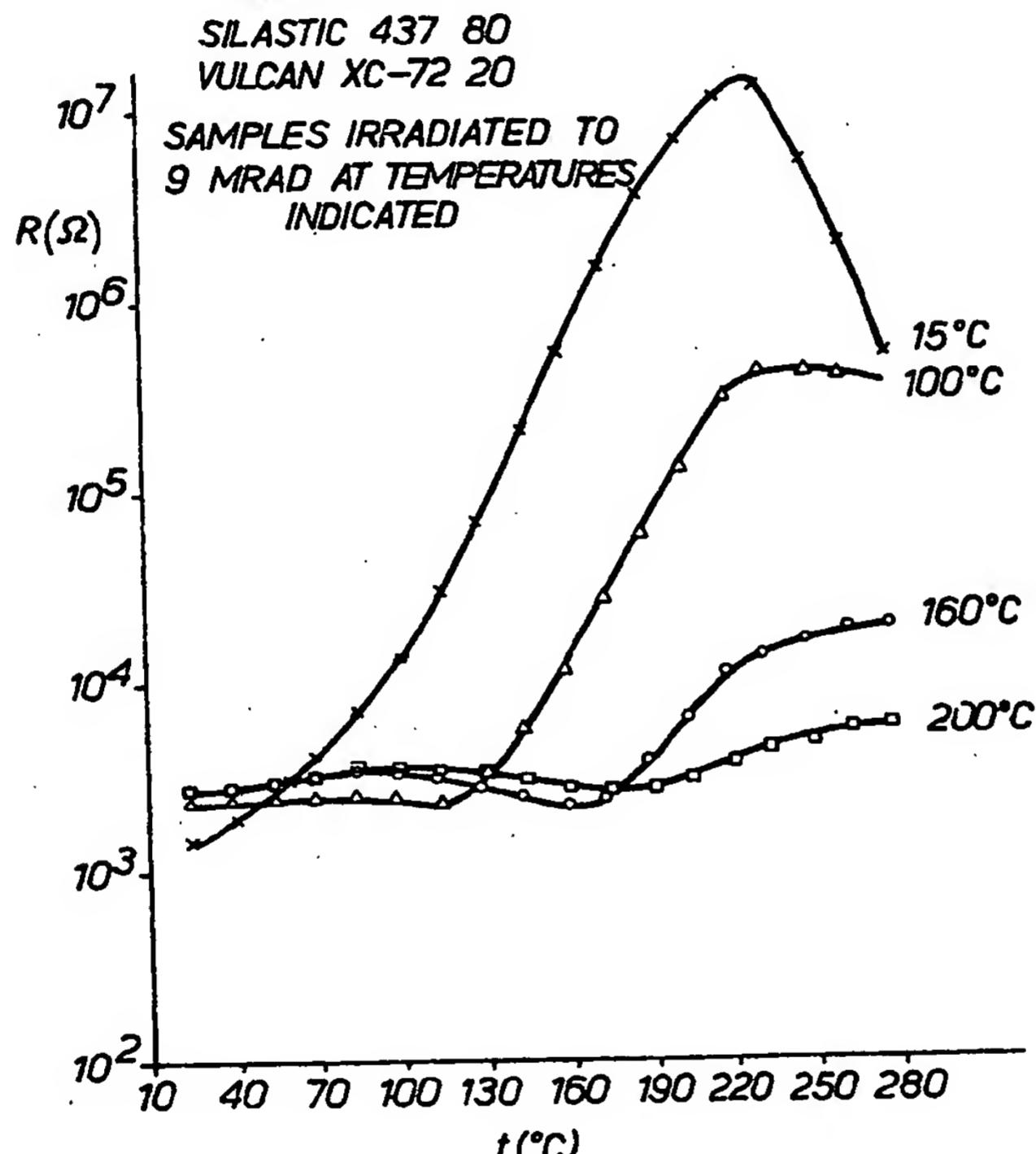
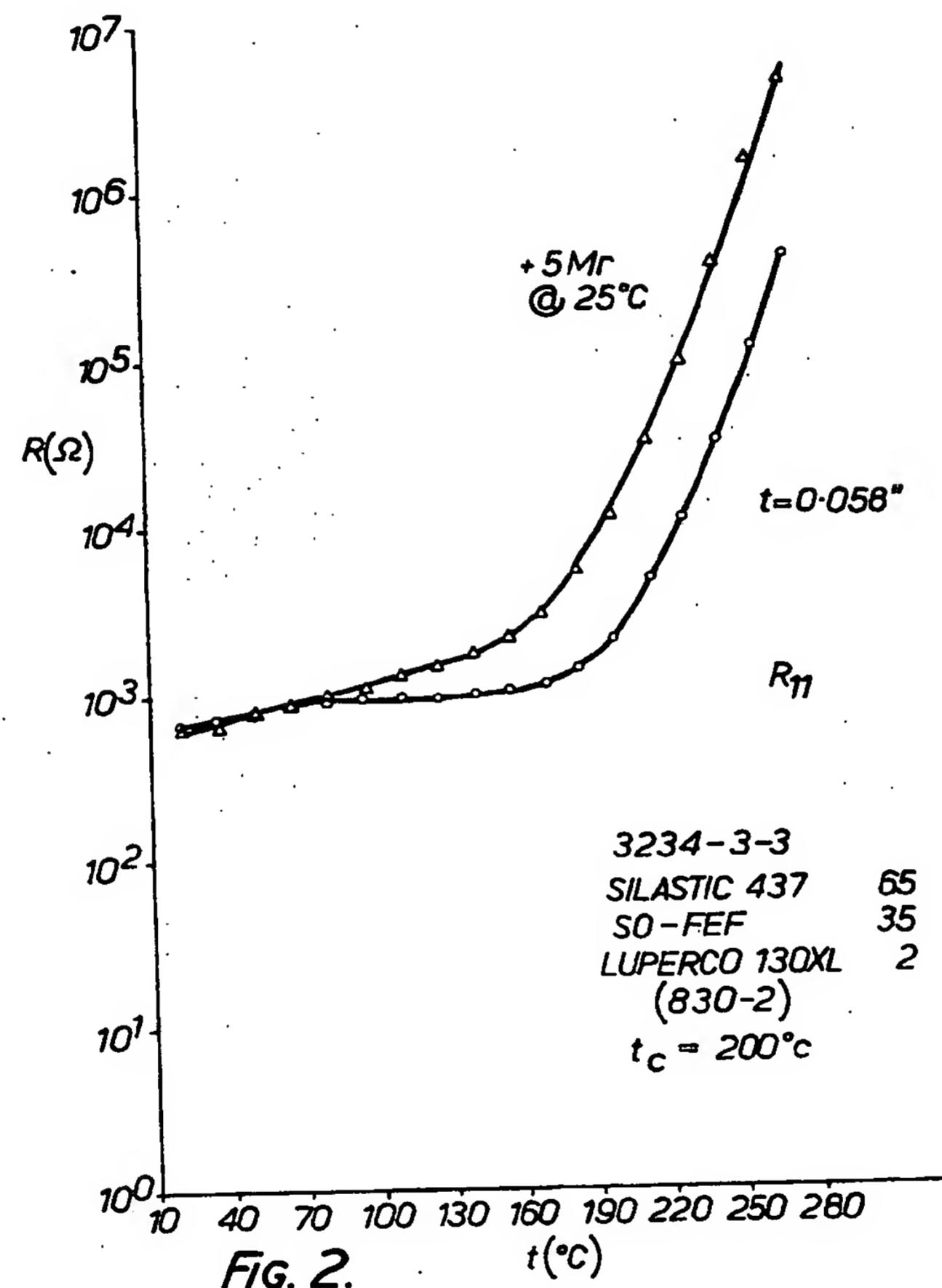


FIG. 1.

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Sheet 2



1595198 COMPLETE SPECIFICATION
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 Sheet 3

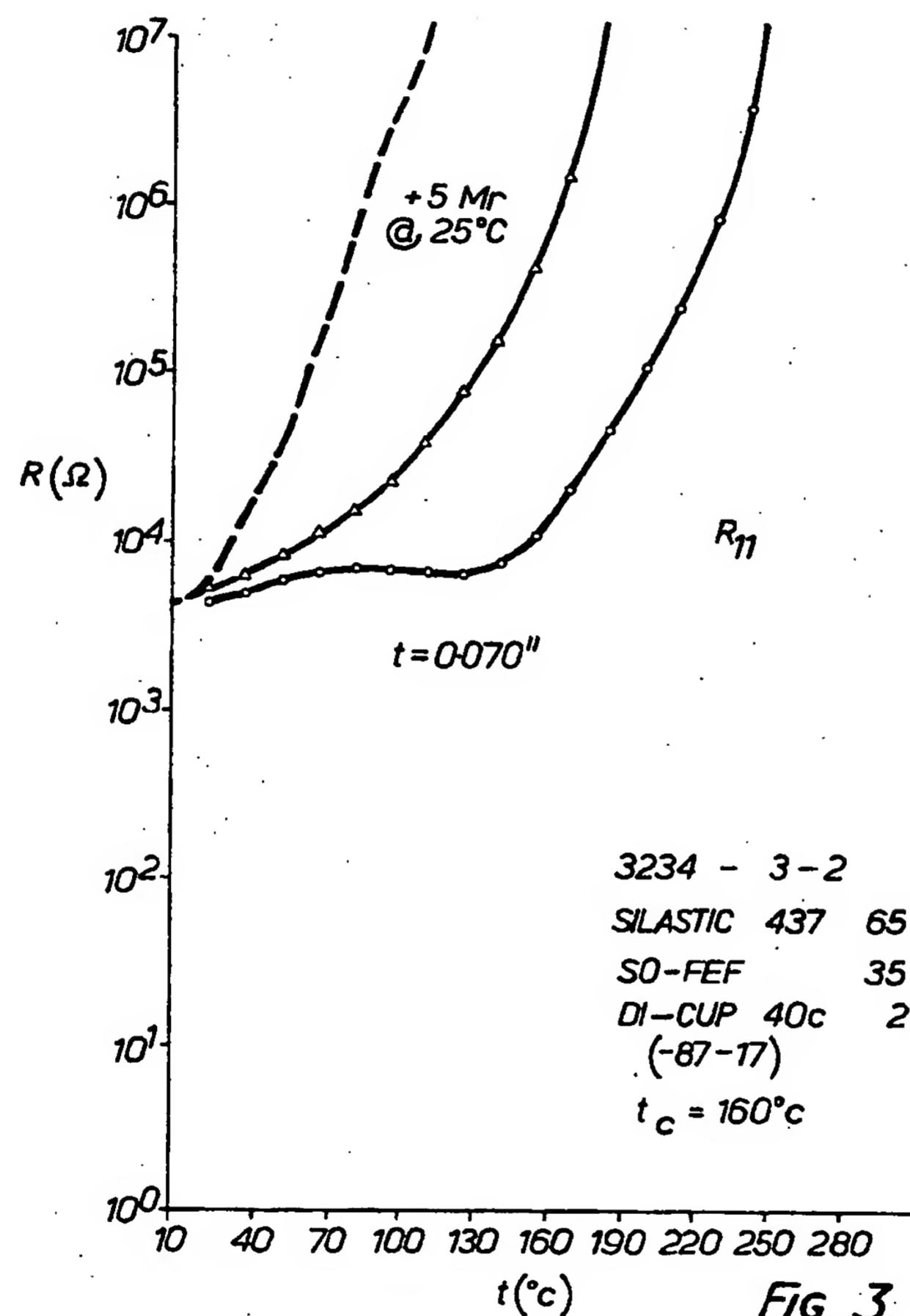


FIG. 3.